

## Short Communications

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### DISCOLORATION RESISTANCE OF NEOPRENE LATEX PRODUCTS ON VULCANIZATION

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Two types of discoloration of the Neoprene latex products are commonly observed. These discolorations are discerned easily in the light coloured products. The first type of discoloration is observed during curing or aging. The second type is apparent during exposure to light. The degree of discoloration among any of the products from general and special purpose latices varied considerably. Out of Du Pont general purposes latices, latex 400 discoloured least upon curing by heat; latices 842A (601A) and 571 are second best. Of special purpose latices, latex 572 appeared to be the best from the standpoint of discoloration on curing. Some of the Neoprene latices even when dried at room temperature showed discoloration. This discoloration intensified on curing. The effect of various compound ingredients on discoloration during curing had been discussed by Carl.<sup>1</sup> Zinc oxide, even non-staining antioxidants and fillers appeared to have little or no effect on curing discoloration, whereas accelerators tended to intensify discoloration. However, the Tepidone (sodium dibutylthiocarbamate)/Thiuram E(tetraethylthiuram disulphide) system causes less discoloration than thiocarbanilide. Stock containing sulphur discoloured more than one without sulphur. Plasticizers aggravated curing discoloration.

It was observed that the products obtained from Neoprene latex 842A containing tetraethylthiuram did not show any curing discoloration. It was further observed that zinc diethyldithiocarbamate was formed during vulcanization. The stock without tetraethylthiuram disulphide discoloured badly. During vulcanization of natural rubber with zinc oxide and tetramethylthiuram disulphide, formation of zinc dimethyldithiocarbamate were reported earlier.<sup>2-4</sup>

#### Experimental

Neoprene latex was compounded using techniques, ingredients and equipments similar to one employed for other latices.<sup>5-8</sup> The Nonex EXN dispersion was made with an equal amount of zinc oxide. The products were obtained by wet coagulant dipping. The coagulated sleeves were cut at the top end, leached in fresh water for 1 hr and dried while on the mandrel. The dried sleeves were stripped from the mandrel and were leached again in fresh water for another 24 hr. These sleeves were air-dried in wire-gauze tray covered with a bleached muslin. The drying period was usually

12-15 days. The degree of dryness was tested by the voltage breakdown test. The dried sleeves were vulcanized in a draught-oven at 150°C for 30 min. All these experiments were carried out under strictly controlled conditions. The vulcanized stock accelerated with tetraethylthiuram disulphide extracted with acetone and the extract was tested for zinc diethyldithiocarbamate as described by Winspear and Auler.<sup>9,10</sup> Typical recipe of the compounded latex and coagulant used are given in Tables 1 and 2.

#### Results and Discussion

The vulcanized sleeves were examined for curing discoloration, colour fastness and tension set as described.<sup>11</sup> The results are given in Table 3.

The sleeves from stock no. 1 showed better resistance to curing discoloration, although tension set and colour fastness were nearly the same as for stock no. 2. It is believed that the resistance to curing discoloration is mainly due to the formation of zinc diethyl dithiocarbamate, which also acts as a good antioxidant.<sup>12</sup> It was further observed that the sleeves obtained from a stock containing thiuram disulphide which had been unstable showed bright and dark spots on vulcanization.

Neoprene is highly regular structure. It is a linear sequence of *trans*-2-chloro-2-butylenylene units, which

TABLE 1. TYPICAL RECIPE OF THE COMPOUNDED LATEX.

Ingredients	Stock no. (dry wt)	
	1	2
Du Pont Neoprene latex 842A (50% S.C.)	100.00	100.00
Vulcastab C paste (50% solution)	2.00	2.00
Water glass (75% solution)	1.66	1.66
Tetraethylthiuram disulphide (50% dispersion)	1.66	Nil
Nonex EXN (25% dispersion)	2.00	2.00
Zinc oxide (50% dispersion)	50.00	50.00
Red dye (33% dispersion)	to required shade	

TABLE 2. RECIPE OF THE COAGULANT.

Ingredients	Weight by parts
Calcium chloride	20.00
Calcium nitrate	20.00
Celite 209	10.00
Talcum	10.00
Methanol	30.00
Water	10.00

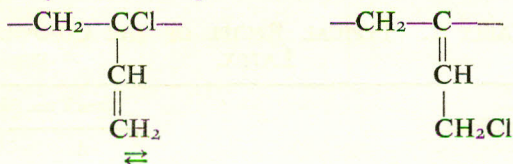
TABLE 3. PHYSICAL PROPERTIES AFTER VULCANIZATION.

Sleeves made from stock no.	Physical appearance	Tension set (%)	Colour fastness	Detection of dithiocarbamate
1	Bright pink	8-9	3	Positive
2	Brownish pink	9-10	2-3	Negative

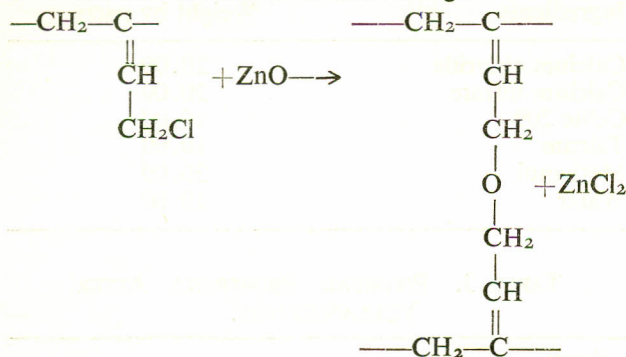
result from *trans*-1,4 addition polymerisation of Chloroprene. Other structural units exist in the polymer-chain resulting from *cis*-1,4; 1,2; and 3,4 additions.<sup>13</sup> The percentage of each structural unit in Neoprene is shown in the chart below.

Type of addition	Formula	Approximate%
<i>Trans</i> -1,4	$\begin{array}{c} \text{---CH}_2 \quad \quad \text{CH} \\ \quad \quad \quad \diagdown \quad / \\ \quad \quad \quad \text{CCl} = \text{C} \\ \quad \quad \quad / \quad \quad \diagdown \\ \quad \quad \quad \text{CH}_2 \text{---} \end{array}$	88-92
<i>Cis</i> -1,4	$\begin{array}{c} \text{---CH}_2 \quad \quad \quad \text{CH}_2 \text{---} \\ \quad \quad \quad \diagdown \quad / \\ \quad \quad \quad \text{CCl} = \text{C} \\ \quad \quad \quad / \quad \quad \diagdown \\ \quad \quad \quad \text{CH} \end{array}$	7-12
1,2	$\begin{array}{c} \text{---CH}_2 \text{---CCl---} \\   \\ \text{CH} \\    \\ \text{CH}_2 \end{array}$	1.5
3,4	$\begin{array}{c} \text{---CH}_2 \text{---CH---} \\   \\ \text{CCl} \\    \\ \text{CH}_2 \end{array}$	1.0

As a result of 1,2 polymerisation, 1.5% chlorine in Neoprene is in an allylic form; it is labile and is believed to be the most active site for cross-linking.<sup>14</sup> It probably exists in equilibrium as indicated below.

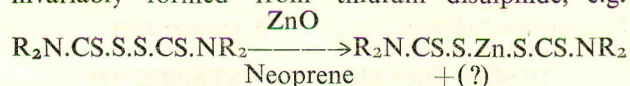


This is considered to be the first step in the vulcanization of Neoprene. It is further reported that without organic accelerator only partial vulcanization occurs with metallic oxides,<sup>14</sup> but the experimental results obtained with stock no. 2 which did not contain any accelerator showed no marked difference in permanent set. Permanent set is taken as the measure of vulcanization. The possible reaction of Neoprene vulcanization with zinc oxide without organic accelerator has been suggested<sup>14</sup> and is given below, but there is no evidence in favour of ether bridge.

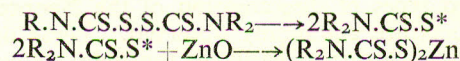


Bisalkylation theory of Neoprene vulcanization<sup>14</sup> and proposed mechanism of the reaction of Neoprene vulcanization with thiourea<sup>15</sup> do not explain the formation of zinc diethyldithiocarbamate. In the

presence of excess zinc oxide under the conditions of vulcanization zinc diethyldithiocarbamate is invariably formed from thiuram disulphide, e.g.



This reaction is known to occur in natural rubber over a range of temperature and concentration of thiuram disulphide and zinc oxide. It has also been demonstrated to occur in diisoprene and geraniol.<sup>16</sup> As the kinetics of both the consumption of tetraethylthiuram disulphide or the formation of zinc diethyldithiocarbamate has not been studied, so it may be speculated that a free radical initiation of thiuram disulphide may occur, which reacts with zinc oxide to form zinc diethyldithiocarbamate



The thiuram fragments which lead to C—C cross-link in natural rubber by radical combination,<sup>17</sup> does not explain the possibility of such reaction in Neoprene. Secondly the permanent set of the stock with or without thiuram disulphide did not show any difference. It is indicated that the thiuram disulphide mostly react with zinc oxide to form dithiocarbamate whereas it is zinc oxide rather than thiuram which is responsible for vulcanization. As no quantitative studies were made so still much remained to be settled.

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